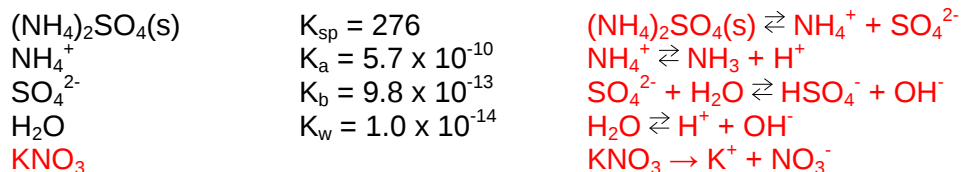


You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures. Activities may be ignored unless specified in a problem.

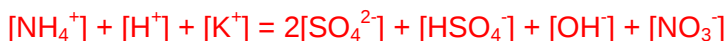
The take-home problem will account for 15 possible points on this exam.

You must complete problem 1.

1. When ammonium sulfate dissolves, both the anion and the cation can participate in acid-base equilibria. Considering all the equilibria active in solution, including the autoprotolysis of water, answer the questions below for a solution that is saturated with ammonium sulfate and also contains 0.10 M potassium nitrate. Do not consider activities.

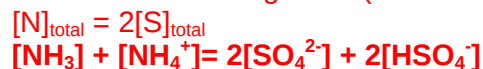


- a. Write the charge balance expression for this system. (4 points)

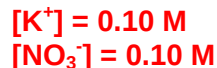


- b. Write three independent mass balance expressions for this system (6 points)

Total concentration of nitrogen = 2(total concentration of sulfur)



Concentrations of Na^+ and NO_3^- are constant



Complete three (3) of problems 2-5. Clearly identify the problem you do not want graded. (10 points each, 30 points total)

2. If I prepare a saturated silver chloride ($K_{sp} = 1.8 \times 10^{-10}$) solution by putting 100 g of AgCl in 10 mL of water and you prepare a saturated silver chloride solution by putting 100 g of AgCl in 100 mL of water, what is the relative concentration of Ag^+ in your solution compared to mine? Clearly explain your reasoning.

Since both solutions are saturated, the silver ion concentrations are identical. It doesn't matter what mass is introduced into the solvent, once the solution is saturated, no additional solute can dissolve.

$$[\text{Ag}^+] = (K_{sp})^{1/2}$$

3. Calculate the pH of a 1.4×10^{-7} F solution of HNO_3 .

Although HNO_3 is a strong acid, the concentration is low enough that we need to consider the contribution of water as a source of H^+ . Start by writing mass and charge balance equations:

$$\text{Charge Balance: } [\text{H}^+] = [\text{NO}_3^-] + [\text{OH}^-]$$

$$\text{Mass Balance: } [\text{NO}_3^-] = 1.4 \times 10^{-7} \text{ M}$$

Substituting the mass balance expression in to the charge balance and using K_w , we can get everything in terms of $[\text{H}^+]$:

$$[\text{H}^+] = 1.4 \times 10^{-7} + K_w/[\text{H}^+] \rightarrow [\text{H}^+]^2 - 1.4 \times 10^{-7} [\text{H}^+] - K_w = 0$$

Solving the quadratic gives $[\text{H}^+] = 1.92 \times 10^{-7} \text{ M}$ or **pH = 6.71**

4. Three primary factors that play a role in determining activity coefficients of ions. Identify each and briefly describe the impact of each factor on the activity of an ion.

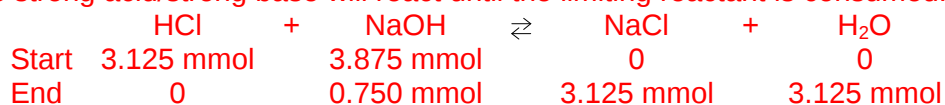
Each affect has an impact on the tendency for an ion to interact with other charged species in solution. Your description should illustrate this.

1. Ion Size or Hydrated diameter (α): The more strongly solvated the ion is (larger α), the less likely it is to interact with competing ions in solution (larger γ).
2. Ionic charge (z): The larger the charge, the greater the electrostatic interaction with competing ions (smaller γ).
3. Ionic strength (μ): The greater the effective concentration of ions in solution, the more opportunities for the ion of interest to interact with competing species (smaller γ).

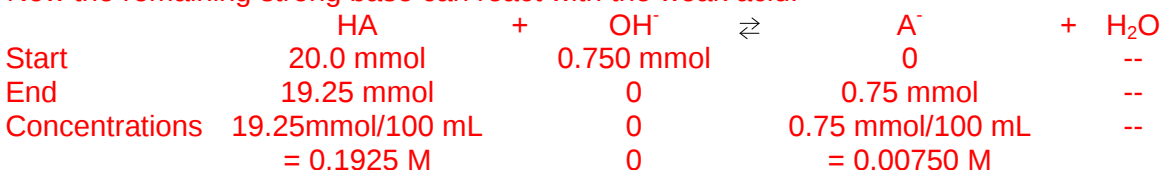
5. A solution is prepared by mixing 0.155 grams sodium hydroxide, 25.0 mL 0.125 M hydrochloric acid and 20.0 mL 1.00 M acetic acid ($pK_a = 4.75$) and diluting to 100.0 mL. What is the pH of the resulting solution? *Do not consider activities.*

To deal with this problem, we first must determine what's left after the strong base NaOH, strong acid HCl and weak acid acetic acid (HA) have the opportunity to react,

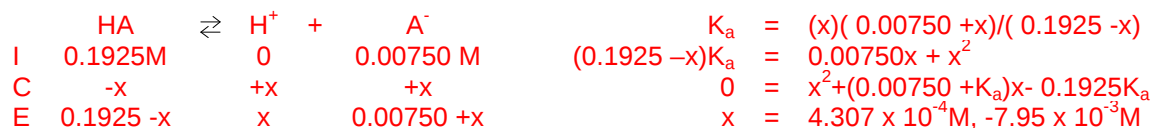
First the strong acid/strong base will react until the limiting reactant is consumed:



Now the remaining strong base can react with the weak acid.



Now solve the equilibrium:



Since a negative value for x makes no chemical sense, the appropriate solution is:

$$x = 4.307 \times 10^{-4}M = [H^+], \text{ or } pH = -\log[H^+] = 3.36$$

Note: Henderson-Hasselbach equation also works and produces pH = 3.34

Do three (3) of problems 6-9. Clearly mark the problem you do not want graded.
(15 pts each, 45 points total.)

I intentionally left LOTS of space for you, I do not expect that you will use all the space.

6. *Using activities*, calculate the fluoride concentration in a saturated solution of calcium fluoride in a solution that contains 0.010 F magnesium nitrate and 0.020 F sodium chloride. The K_{sp} for calcium fluoride is 3.2×10^{-11} , assume that all other salts are soluble. You may ignore the autoprotolysis of water and any acid-base character of the ions in solution.

	CaF_2	=	Ca^{2+}	+	2F^-
I	--		0		0
C	--		+x		+2x
E	--		x		2x

$$K_{sp} = A_{\text{Ca}^{2+}}(A_{\text{F}^-})^2 = \gamma_{\text{Ca}^{2+}}[\text{Ca}^{2+}](\gamma_{\text{F}^-}[\text{F}^-])^2 = \gamma_{\text{Ca}^{2+}}x(\gamma_{\text{F}^-}2x)^2 = \gamma_{\text{Ca}^{2+}}(\gamma_{\text{F}^-})^2 4x^3$$

Since K_{sp} is so small, little dissolution of CaF_2 will occur, and the ionic strength will be determined by the concentrations of $\text{Mg}(\text{NO}_3)_2$ and NaCl .

$$\mu = \frac{1}{2}\{[\text{Mg}^{2+}](+2)^2 + [\text{NO}_3^-](-1)^2 + [\text{Na}^+](+1)^2 + [\text{Cl}^-](-1)^2\} \frac{1}{2}$$

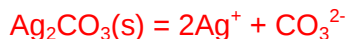
$$\mu = \frac{1}{2}(0.010\text{M}(4) + 0.020\text{M}(1) + 0.020\text{M}(1) + 0.020\text{M}(1)) = 0.050\text{M}$$

Using the table of activity coefficients at this ionic strength, $\gamma_{\text{Ca}^{2+}} = 0.485$, $\gamma_{\text{F}^-} = 0.81$.
(The Debye-Huckel equation gives similar values.)

Therefore, the expression to solve is: $3.2 \times 10^{-11} = (0.485)(0.81)^2 4x^3$

Given these values, and solving for x, $x = 2.93 \times 10^{-4}\text{M}$, $[\text{F}^-] = 2x = 5.86 \times 10^{-4}\text{M}$

7. What is the silver ion concentration in a solution prepared by mixing 50.0 mL of 0.496 M silver nitrate with 50.0 mL of 0.387 M sodium carbonate? The K_{sp} of silver carbonate is 8.1×10^{-12} . You may ignore activities, autoprotolysis and the acid-base behavior of carbonate ion.



First find the composition of the solution after Na_2CO_3 and AgNO_3 have had the opportunity to react to form some Ag_2CO_3 . What is the limiting reagent?

$$50.0 \text{ mL} \times \frac{0.496 \text{ mol AgNO}_3}{1 \text{ L}} \times \frac{1 \text{ mol CO}_3^{2-}}{2 \text{ mol AgNO}_3} = 12.4 \text{ mmol CO}_3^{2-} \text{ needed}$$

$$50.0 \text{ mL} \times \frac{0.387 \text{ mol Na}_2\text{CO}_3}{1 \text{ L}} \times \frac{1 \text{ mol CO}_3^{2-}}{1 \text{ mol Na}_2\text{CO}_3} = 19.35 \text{ mmol CO}_3^{2-} \text{ present}$$

So, Ag is the limiting reagent and $(19.35 - 12.4) = 6.95 \text{ mmol CO}_3^{2-}$ will remain after reaction, producing a carbonate concentration of $6.95 \text{ mmol}/100. \text{ mL} = 0.0695 \text{ M}$. Now ICE table!

	Ag_2CO_3	=	2Ag^+	+	CO_3^{2-}
i	-		0		0.0695 M
c	-		+2x		+x
e	-		2x		0.0695 + x

$$K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = (2x)^2(0.0695 + x)$$

We can simplify things if we assume $x \ll 0.0695$, then $K_{sp} = (2x)^2(0.0695)$

$$x = \left[\frac{K_{sp}}{4(0.0695)} \right]^{1/2} = 5.40 \times 10^{-6} \text{ M}$$

$$[\text{Ag}^+] = 2x = 1.08 \times 10^{-5} \text{ M}$$

Checking our assumption, to 3 sig figs, $0.000108 < 0.0695$!

8. Given your unnatural passion for solution equilibria, you have been assigned the task of teaching a chemistry class about the role of charge and mass balance in equilibrium systems. Briefly define and illustrate each term, using a solution containing 0.020 M HNO₃, 0.010 M KNO₃ and 0.10 M oxalic acid (H₂C₂O₄, pK_{a1} = 1.252, pK_{a2} = 4.266) as an example. Your answer must include example mass and charge balance expressions.

Mass Balance illustrates the conservation of mass. (total moles of an atom at any time must be the same as the total moles of the atom introduced)

Charge Balance is a result of the necessity for the solution to be electrically neutral.

Possible Mass Balance:

$$0.10 \text{ M} = [\text{H}_2\text{C}_2\text{O}_4] + [\text{HC}_2\text{O}_4^-] + [\text{C}_2\text{O}_4^{2-}]$$

$$0.030 \text{ M} = [\text{NO}_3^-]$$

$$0.010 \text{ M} = [\text{K}^+]$$

$$[\text{H}^+] = 0.020\text{M} + [\text{HC}_2\text{O}_4^-] + 2[\text{C}_2\text{O}_4^{2-}] + [\text{OH}^-]$$

Charge Balance:

$$[\text{H}^+] + [\text{K}^+] = [\text{NO}_3^-] + [\text{HC}_2\text{O}_4^-] + 2[\text{C}_2\text{O}_4^{2-}] + [\text{OH}^-]$$

9. Buffers.

- a. How many grams of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ must be added to 400 mL of 0.200 M H_3PO_4 to give a buffer of pH 4.30 (Assume no volume change)? (For H_3PO_4 , pK_a 's = 2.148, 7.198 and 12.375) (8 points)

First, determine the ratio of A^-/HA needed for pH 4.50 by rearranging the Henderson Hasslebach equation:

$$\text{pH} = 2.148 + \log \frac{\text{mol H}_2\text{PO}_4^-}{\text{mol H}_3\text{PO}_4}$$

So,

$$\frac{\text{mol A}^-}{\text{mol HA}} = 10^{\text{pH}-\text{pK}_a} = 10^{4.30-2.148} = 142$$

Therefore, we need 142 times as much $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ as H_3PO_4 . We have 0.080 mol H_3PO_4 , so we need $142 \times 0.080 = 11.36$ mol $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. The molar mass of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ is 156.01 g/mol. So, we need $11.36 \text{ mol} \times (156.01 \text{ g/mol}) = 1770 \text{ g}$! That is a lot! Given the ratio of conjugate base to acid of 142, this will not be an effective buffer!

Note: This huge number is a result of me having a target pH of 4.30 instead of 2.30, which was my intent, but I didn't discover the typo before the exam! A pH of 2.30 would have required 17.7 grams of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. A much more reasonable amount!

- b. What would the pH of this buffer be after the addition of 0.1 mol NaOH? (Assume no volume change.) (7 points)

The addition of NaOH would consume any strong or weak acid present in the system. Since we are starting with 0.080 mol H_3PO_4 and adding 0.1 mol NaOH, all of the H_3PO_4 would be converted to H_2PO_4^- , producing a total of $(11.36 + 0.08 = 11.44 \text{ mol H}_2\text{PO}_4^-)$ and 0.02 mol NaOH would still remain. Since H_2PO_4^- is also a weak base, the remaining NaOH would react with it to consume 0.02 mol H_2PO_4^- , leaving 11.42 mol and producing 0.02 mol HPO_4^{2-} . We therefore would have a buffer (albeit a poor one) using K_{a2} .

$$\text{pH} = 7.198 + \log \frac{\text{mol HPO}_4^{2-}}{\text{mol H}_2\text{PO}_4^-}$$

$$\text{pH} = 7.198 + \log \frac{0.02 \text{ mol}}{11.42 \text{ mol}}$$

$$\text{pH} = 4.44$$

Starting with the pH 2.3 system, we are starting with 0.080 mol H_3PO_4 and adding 0.1 mol NaOH, all of the H_3PO_4 would be converted to H_2PO_4^- , producing a total of $(0.1136 + 0.08 = 0.1936 \text{ mol H}_2\text{PO}_4^-)$ and 0.02 mol NaOH would still remain. Since H_2PO_4^- is also a weak base, the remaining NaOH would react with it to consume 0.02 mol H_2PO_4^- , leaving 0.1736 mol and producing 0.02 mol HPO_4^{2-} . We therefore would have a buffer using K_{a2} .

$$\text{pH} = 7.198 + \log \frac{0.02 \text{ mol HPO}_4^{2-}}{0.1736 \text{ mol H}_2\text{PO}_4^-} = 6.26$$

Possibly Useful Information

$-\log \gamma = \frac{0.51z^2\sqrt{\mu}}{1 + \alpha\sqrt{\mu}/305}$	$\mu = \frac{1}{2} \sum_i c_i z_i^2$
$\Delta G = \Delta H - T\Delta S = -RT \ln K$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_w = 1.00 \times 10^{-14}$	$\text{pH} = -\log[\text{H}^+]$
$\text{pH} = \text{pK}_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$	$\text{pH} = \frac{1}{2} (\text{pK}_{a1} + \text{pK}_{a2})$
$K_a K_b = K_w = 1.00 \times 10^{-14}$	$\alpha_{\text{H}_2\text{A}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+] K_{a1} + K_{a1} K_{a2}}$
$\alpha_{\text{A}^{2-}} = \frac{K_{a1} K_{a2}}{[\text{H}^+]^2 + [\text{H}^+] K_{a1} + K_{a1} K_{a2}}$	

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	INERT GASES	
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122																
11 Na 22.9898	12 Mg 24.312																
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	+89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
--------------------	---------------------	--------------------	-------------------	--------------------	--------------------	--------------------	---------------------	--------------------	---------------------	--------------------	---------------------	--------------------	--------------------

† Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)
---------------------	-------------------	-------------------	-------------------	-------------------	-------------------	-------------------	-------------------	-------------------	-------------------	--------------------	--------------------	--------------------	--------------------

Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α , pm)	Ionic strength (μ , M)				
		0.001	0.005	0.01	0.05	0.1
CHARGE = ± 1						
H ⁺	900	0.967	0.933	0.914	0.86	0.83
(C ₆ H ₅) ₂ CHCO ₂ ⁻ , (C ₃ H ₇) ₄ N ⁺	800	0.966	0.931	0.912	0.85	0.82
(O ₂ N) ₃ C ₆ H ₂ O ⁻ , (C ₃ H ₇) ₃ NH ⁺ , CH ₃ OC ₆ H ₄ CO ₂ ⁻	700	0.965	0.930	0.909	0.845	0.81
Li ⁺ , C ₆ H ₅ CO ₂ ⁻ , HOC ₆ H ₄ CO ₂ ⁻ , ClC ₆ H ₄ CO ₂ ⁻ , C ₆ H ₅ CH ₂ CO ₂ ⁻ , CH ₂ =CHCH ₂ CO ₂ ⁻ , (CH ₃) ₂ CHCH ₂ CO ₂ ⁻ , (CH ₃ CH ₂) ₄ N ⁺ , (C ₃ H ₇) ₂ NH ₂ ⁺	600	0.965	0.929	0.907	0.835	0.80
Cl ₂ CHCO ₂ ⁻ , Cl ₃ CCO ₂ ⁻ , (CH ₃ CH ₂) ₃ NH ⁺ , (C ₃ H ₇)NH ₃ ⁺	500	0.964	0.928	0.904	0.83	0.79
Na ⁺ , CdCl ⁺ , ClO ₂ ⁻ , IO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HSO ₃ ⁻ , H ₂ AsO ₄ ⁻ , Co(NH ₃) ₄ (NO ₂) ₂ ⁺ , CH ₃ CO ₂ ⁻ , ClCH ₂ CO ₂ ⁻ , (CH ₃) ₄ N ⁺ , (CH ₃ CH ₂) ₂ NH ₂ ⁺ , H ₂ NCH ₂ CO ₂ ⁻	450	0.964	0.928	0.902	0.82	0.775
⁺ H ₃ NCH ₂ CO ₂ H, (CH ₃) ₃ NH ⁺ , CH ₃ CH ₂ NH ₃ ⁺	400	0.964	0.927	0.901	0.815	0.77
OH ⁻ , F ⁻ , SCN ⁻ , OCN ⁻ , HS ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , IO ₄ ⁻ , MnO ₄ ⁻ , HCO ₂ ⁻ , H ₂ citrate ⁻ , CH ₃ NH ₃ ⁺ , (CH ₃) ₂ NH ₂ ⁺	350	0.964	0.926	0.900	0.81	0.76
K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , NO ₂ ⁻ , NO ₃ ⁻	300	0.964	0.925	0.899	0.805	0.755
Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Tl ⁺ , Ag ⁺	250	0.964	0.924	0.898	0.80	0.75
CHARGE = ± 2						
Mg ²⁺ , Be ²⁺	800	0.872	0.755	0.69	0.52	0.45
CH ₂ (CH ₂ CH ₂ CO ₂ ⁻) ₂ , (CH ₂ CH ₂ CH ₂ CO ₂ ⁻) ₂	700	0.872	0.755	0.685	0.50	0.425
Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺ , C ₆ H ₄ (CO ₂ ⁻) ₂ , H ₂ C(CH ₂ CO ₂ ⁻) ₂ , (CH ₂ CH ₂ CO ₂ ⁻) ₂	600	0.870	0.749	0.675	0.485	0.405
Sr ²⁺ , Ba ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , S ₂ O ₄ ²⁻ , WO ₄ ²⁻ , H ₂ C(CO ₂ ⁻) ₂ , (CH ₂ CO ₂ ⁻) ₂ , (CHOHCO ₂ ⁻) ₂	500	0.868	0.744	0.67	0.465	0.38
Pb ²⁺ , CO ₃ ²⁻ , SO ₃ ²⁻ , MoO ₄ ²⁻ , Co(NH ₃) ₅ Cl ²⁺ , Fe(CN) ₅ NO ²⁻ , C ₂ O ₄ ²⁻ , Hcitrate ²⁻	450	0.867	0.742	0.665	0.455	0.37
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , S ₂ O ₆ ²⁻ , S ₂ O ₈ ²⁻ , SeO ₄ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻	400	0.867	0.740	0.660	0.445	0.355
CHARGE = ± 3						
Al ³⁺ , Fe ³⁺ , Cr ³⁺ , Sc ³⁺ , Y ³⁺ , In ³⁺ , lanthanides ^a	900	0.738	0.54	0.445	0.245	0.18
citrate ³⁻	500	0.728	0.51	0.405	0.18	0.115
PO ₄ ³⁻ , Fe(CN) ₆ ³⁻ , Cr(NH ₃) ₆ ³⁺ , Co(NH ₃) ₆ ³⁺ , Co(NH ₃) ₅ H ₂ O ³⁺	400	0.725	0.505	0.395	0.16	0.095
CHARGE = ± 4						
Th ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺	1 100	0.588	0.35	0.255	0.10	0.065
Fe(CN) ₆ ⁴⁻	500	0.57	0.31	0.20	0.048	0.021

a. Lanthanides are elements 57–71 in the periodic table.

SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937**, 59, 1675.